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Practical Experience in Analysis of Organic Compounds in Ambient Air Using Canisters and Sorbents

Radian Corp., Research Triangle Park, NC

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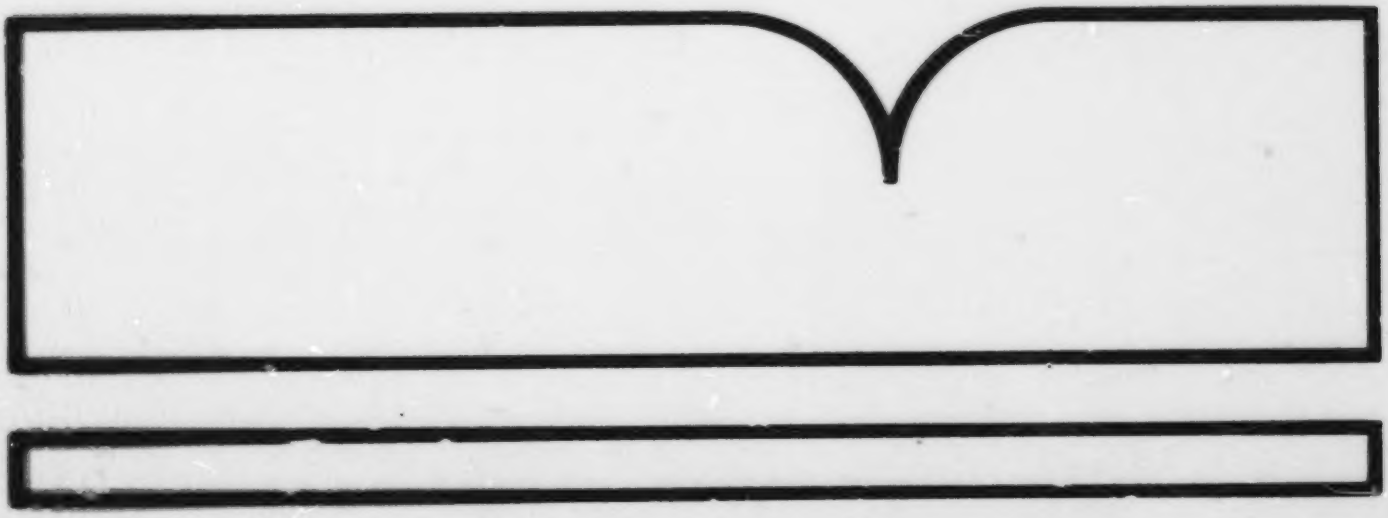

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16. ABSTRACT

Generation of accurate ambient air VOC pollutant measurement data as a basis for regulatory decisions is critical. Numerous methods and procedures for sampling and analysis are available from a variety of sources. By comparison with water analysis, however, air analysis suffers from a lack of specific methods and applications experience. Air methods available through the Environmental Protection Agency are contained in the "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air."[1] Some of the methods in this Compendium are developed and validated only in a single laboratory. Some of the Compendium methods represent a synthesis of the procedures performed in a number of laboratories. The range of applicability of the methods is defined only in general outline, with very little specific data available to assess the performance of the total methodology for a large number of compounds. There are many criteria which must be considered in the selection of methodology for ambient air sampling and analysis. Both canisters and sorbents may be used for Volatile Organic Compounds. Both approaches have strengths and weaknesses. There is considerable latitude regarding selection of analytical methodology: mass spectrometry, high performance liquid chromatography, and gas chromatography with a variety of detectors are used at various times for various reasons. Even the exact type of measurement to be taken will vary according to program needs and the ultimate use of the data. The quality of the air measurement data is also a function of the skill, competence, and experience of both the field study collection team and the laboratory which is executing the methodology. This paper presents examples of Radian's experience with ambient air measurement techniques.

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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INTRODUCTION

There is widespread interest in the environmental analytical community in the generation of accurate measurements of volatile organic compounds in ambient air. The imminent passage of Clean Air legislation has created a demand for accurate air toxics measurement data. Both sampling and analysis are crucial to the generation of accurate data. However, the analytical community faces unique problems in meeting the demand for data. The water matrix has established EPA methods which specify exact procedures to be followed, exact quality assurance criteria to be met, and a list of compounds for which the methodology has been validated. Air methods are not as detailed or specific and, in general, have not been extensively validated for specified lists of compounds.

A major problem facing the analytical community is selection of appropriate methods for compounds of interest. As a service to users, fourteen methods for measuring various toxic organic compounds in ambient air (Methods TO-1 through TO-14) have been compiled and published by EPA in a Compendium.[1] These methods are presented in a standardized format and have been extensively peer-reviewed. They have not been subjected to collaborative laboratory testing and are not certified or officially endorsed by EPA. Once the general methodology has been selected, according to whatever criteria the person selecting the methodology applies, various alternatives must be considered based on the particular application in the area of air sampling and analysis. The air sampling/analytical method most commonly cited, TO-14, provides guidance on techniques rather than explicit procedures with established detection limits and quality criteria. A further problem often arises with the generation of the data appropriate for the intended use: Are accurate, quantitative data necessarily required for specific compounds or is semi-quantitative information on a broad range of possible compounds desired? Are speciated data required at all?

Tables 1-5 summarize information regarding the various sampling media which are commonly used in ambient air sampling and analysis. The methods which use these matrices are summarized, the range of applicability of the methods is described, and the advantages, disadvantages, and problems with the media are shown.

Use of Sorbents for Ambient Air Sampling and Analysis

Solid sorbents, including Tenax GC®, various forms of carbon, XAD-2®, and inorganic materials have been used in various applications for at least two decades. The sorbents with the longest history and broadest application are Tenax GC® and carbon. Successful use of any sorbent in a sampling and analytical methodology requires that: 1) the sorbent have a know capacity for the compounds of interest which is not exceeded in field sampling; 2) an accurate analysis can be performed when the compound has been adsorbed in the field; 3) the amount of analyte calculated from the analysis is an accurate reflection of the amount of the compound present in the air which was sampled; 4) the sorbent can be adequately cleaned and protected from contamination.

Volatile organic compounds have a wide range of breakthrough volumes on any selected sorbent. The breakthrough volume is that sample volume at which the amount of compound collected stops being representative of the volume of air sampled. When the breakthrough volume has been reached or exceeded, collection of additional sample volume will not increase the concentration of target analyte on the sorbent. Breakthrough volumes are not always available from the literature for all of the compounds of interest. Tenax GC® is a good example. Method TO-1 lists approximately twenty compounds with their estimated breakthrough volumes on Tenax GC®. Estimated breakthrough volumes for the compounds discussed in the method range from 6 to 300 liters/gram. It is, therefore, entirely possible that a compound spiked on Tenax GC® can be analyzed accurately in the laboratory; but, if a typical 15-20 liter sample is taken, breakthrough for this compound may occur in the field resulting in nonrepresentative samples.

To determine whether breakthrough has occurred, the user of the methodology has several choices. Sampling can be performed with a backup tube (for Tenax® sampling either all-Tenax GC® or a combination

of Tenax GC® and charcoal). The backup tube can be analyzed separately in order to verify whether or not a compound of interest has broken through the original sampling tube. If breakthrough has occurred, all data for a given compound should be qualified as "minimum values": that is, the actual value of the compound in the field will be at least the value determined in the analysis. If steady-state input is assumed, a surge at the start of sampling will cause the "minimum value" to be an under estimate. If a high concentration was sampled just before the end of the sampling period the "minimum value" may only be slightly less than the true concentration. This "minimum value" will probably fail to meet the needs of most sampling/analytical programs which will require accurate and defensible data.

Another way of resolving the problem of breakthrough on solid sorbents is by designing a sampling strategy with distributed air volumes. Distributed air volumes can be understood as follows. If breakthrough has not occurred with the sampling media, the amount of a given compound observed will be a function of the volume of air sampled. For example, if a value of x is obtained with a ten-liter sample, a value of 2x should be obtained with a twenty-liter sample collected over the same time period from the same body of air. Investigators have used from two to four different sampling volumes to evaluate breakthrough in field applications of sorbent sampling. Using any form of distributed volumes helps verify the accuracy of quantitative values, but the cost of the additional samples can quadruple the analysis costs to the program. If a data rejection rate from the use of the distributed volume technique is high, resampling and analysis by an alternative technique may be warranted. In any case, the distributive air volume technique provides solid experimental verification of the validity of data points which are not rejected. However, it must be emphasized that the distributed air volume approach is a diagnostic technique and NOT a corrective measure.

Sorbent Preparation and Cleaning

An additional problem with all sorbents is obtaining and maintaining cleanliness. Sorbents are used because they adsorb organic compounds well. To have a valid determination, the sorbents must be clean prior to use so that analysis of blanks does not show significant concentrations of compounds of interest. Every laboratory which cleans and prepares sorbents for field use must have Standard Operating Procedures and strict quality control and quality assurance procedures to ensure that sorbent sampling tubes are clean and properly protected when they go to the field. Retention of prepared sorbent tubes for quality control purposes is a must. These tubes must be from the same batch of sorbent used for actual sampling. These tubes serve as laboratory blanks to monitor the occurrence of contamination in the shipping/handling process. Clean tubes from the same batch of sorbent should be shipped to and from the field with the sampling tubes to serve as field and trip blanks. Strict procedures must be followed in the field for avoiding any contact, however remote, with organic solvents. Strict procedures must also be followed for handling sorbents in order to avoid contamination. Every laboratory performing analysis of sorbents has a collection of horror stories about contaminated sorbent tubes (often contaminated with methylene chloride, benzene, or toluene) which caused extensive and expensive field studies to be invalidated. Simple mistakes occur which invalidate results: storing or packing the sorbent in an area where solvents were in use, or some solvent was in use in an adjacent laboratory when analysis was being performed, etc. Sorbent medium is always ready to adsorb organic compounds, and if organic solvent is present in the vicinity of sorbent preparation the sorbent will reflect the contamination.

To avoid contamination, sorbents must be stored in air-tight containers, preferably with a layer of clean activated carbon in the bottom of the container. If the container is truly air-tight, the carbon is not necessary. For ambient monitoring, common practice requires each individual sampling tube to be stored in a clean glass container with a Teflon®-lined screw cap (a layer of charcoal may also be used in the individual storage tubes). The glass containers should then be stored in another air-tight container, securely braced to avoid breakage during shipment. Once the exposed tubes have been received in the laboratory, they should be stored under subambient temperature conditions in a refrigerator/freezer which does not contain solvents and which has never contained solvents. However, refrigerated storage will almost invariably result in the observation of Freons in the analysis.

Artifacts

All sorbents experience some form of artifact problem. Common artifacts on Tenax GC® are benzene, toluene, styrene, phenolic compounds, and alkylstyrenes up to three or four carbon substitution. Artifacts, broadly speaking, are the result of improper cleaning, improper handling, chemical reaction or thermal breakdown of the sorbent. Benzene, toluene, and alkylated aromatic compounds are very frequently compounds of analytical interest. Distributed-volume studies are essential to distinguish artifacts: a compound which is present in the air being sampled should show an increase in concentration with volume sampled, whereas an artifact should not increase.

Tenax GC®

Table 1 focuses on the use of Tenax GC® as an example of sorbent used for ambient air sampling. Tenax GC® is poly (2,6-diphenyl phenylene oxide), a porous polymer with a large surface area, and has a wide range of applications. This polymer is used in source sampling, in the Volatile Organic Sampling Train (VOST) method (EPA Method 5040).[2] Another application of Tenax GC® is sampling and analysis for volatile organic compounds in ambient air according to EPA Method TO-1. Tenax GC® may be applied to determine volatile, nonpolar organic compounds such as aromatic hydrocarbons and chlorinated hydrocarbons with boiling points in the range of 80°C to 200°C. However, Method TO-1 states that not all compounds which fall into this category can be determined. Experience by many laboratories including those at Radian shows that artifacts like benzene and toluene can complicate the interpretation of data from Tenax GC®. The user is responsible to validate the methodology for the compounds of interest.

There is also no standard configuration for Tenax-GC® sampling tubes. Every laboratory which has developed sorbent analysis capability has a sampling tube configuration which suits their sampling and analytical equipment and techniques. Sampling tubes may be glass or stainless steel. Glass tubes may be 3/8 in. straight sided or bulb-shaped with 1/4 in. glass tubing on both ends. Stainless steel tubes are usually 12.7 mm ID and 100 mm long; the only universal criterion for tubes of all shapes is that they contain approximately 1.5 g of Tenax®. Desorption equipment can have a problem with accommodating the range of sampling tubes which may be used. Laboratories which are required to analyze samples from a variety of sources must be inventive in the selection or design of desorption apparatus. For this situation, the flexibility allowed by the TO methods allows the laboratory to use whatever equipment will perform efficient and reproducible desorption, whether they purchase the equipment or design and construct it themselves.

Carbon Molecular Sieve

Carbon molecular sieve (Table 3) is used in Method TO-2, for compounds which exhibit low breakthrough volumes on Tenax®. This sorbent material challenges an analytical system because it must be desorbed at 350°-400°C, far higher than Tenax®. In addition, results from this sorbent medium are less reproducible than results with other media: the method cites standard deviations for a list of eleven compounds for which the methodology was developed ranging from 3 to 37 ng/L. However, compounds which must be analyzed by TO-2 can also be analyzed using the TO-14 methodology, so there is a choice of applicable methodology. The TO-14 methodology also encompasses most of the compounds for which TO-1 is appropriate. The carbon molecular sieve sorbent technique may use commercially available standards prepared in methanol or standards from a static dilution bulb. Like most sorbents, carbon molecular sieve is easily contaminated and must be handled very carefully to avoid invalidating a sampling/analysis effort. If Tenax-GC® is used for TO-1 compounds and carbon molecular sieve is used for appropriate TO-2 sampling and analysis, two different sets of samples must be taken and analyzed to cover a complete range of volatile organic compounds.

Polyurethane Foam (PUF)

Polyurethane foam (PUF) (Table 4) is used to sample semivolatile organic compounds in ambient air. The general list of applicable compounds includes organochlorine pesticides (TO-4), polychlorinated

biphenyls (TO-9), polychlorinated dibenzodioxins and dibenzofurans (TO-10), and polynuclear aromatic hydrocarbons (TO-13). The PUF adsorbs organic compounds from air, which are then solvent extracted for analysis. The extractive process represents a sample dilution, but PUF can be used in high volume (approximately 200-300 L/min) sampling so sufficient sample can usually be collected to meet analytical detection limits. PUF has the same problems as other sorbent media: careful cleanup in preparation for field use is a painstaking and difficult process, and contamination occurs very easily. The collection efficiency of PUF for any given compound which is not directly cited in one of the applicable methods must be determined by the user. There are commercial organizations which prepare PUF for field use, and the field-ready material can be purchased or rented by the user.

However, polyurethane foam suffers from problems with stability, and has a low capacity for light weight semivolatile compounds. In Radian laboratories, we have observed problems with breakthrough for mono- and di-chlorinated biphenyls and two- and three-ring aromatic compounds. Polyurethane foam is only good for the specific compounds for which validation data are available; universal applicability of this sorbent medium to a wide range of semi-volatile organic compounds is questionable. Also, the sampling equipment which is required to sample effectively with polyurethane foam (high volume samplers) is moderately expensive.

XAD-2® Sampling Medium

XAD-2® (Table 5) is a polystyrene divinylbenzene adsorbent with a large surface area and porosity. This polymer is used in the Semi-VOST method for source sampling and in Method TO-13 together with PUF for polynuclear aromatic hydrocarbons (PAHs). The use of XAD-2® in ambient air sampling and analysis for semivolatile organic compounds other than PAH has no status as an EPA method, but the resin is used in the environmental analytical community and by EPA for ambient air quality research programs. XAD-2® sorbent resin has all the problems inherent in sorbents: cleanup in preparation for field use is a painstaking process, contamination of the resin occurs readily, and extensive artifacts are encountered in the analytical process. In the case of XAD-2®, there are various companies which prepare the resin for field use and sell the prepared resin. There is a fairly extensive database available to address sampling efficiencies for organic compounds and some recovery and detection limit data available for semivolatile organic compounds based on research done by EPA in the late 1970's. Recent efforts to clean XAD-2® for ambient air use have met with success.

Little information is available about sampling efficiency and breakthrough volume for XAD-2® used to sample ambient air. A laboratory using this sorbent medium would need to establish these parameters in order to generate valid, representative data. All of the precautions and checks used to establish retention volumes and accurate sample collection for volatile organic collection sorbents hold for XAD-2® and semivolatile organic collection. The resin is extracted rather than thermally desorbed, so extracts can be diluted or concentrated according to the requirements of a given sample or program. Also, use of an extract implies that re-analysis is possible if necessary. The XAD-2® resin traps polar semivolatile compounds, and these types of compounds can be extracted efficiently with appropriate attention to solvent and pH used for extraction. XAD-2® is potentially applicable to a wide range of compounds (compounds such as polycyclic aromatic hydrocarbons, polychlorinated dibenzodioxins and dibenzofurans, for example). Additional validation is necessary to make this medium more readily accepted for the sampling and analysis of semivolatile organic compounds in ambient air.

Use of SUMMA®-Passivated Canisters

SUMMA®-passivated canisters (Table 2) present an alternative to sorbents for sampling volatile and semivolatile compounds. Canisters have as long a history as solid sorbents for ambient air sampling. However, their use over the past 5 to 7 years has increased dramatically.

The methods which require the use of canisters are TO-12 and TO-14. These two methods produce two different types of data: TO-14 focuses on the production of accurate numbers for individual species, while TO-12 produces a single number characteristic of non-methane organic compounds. The primary uses of data generated in ambient air sampling and analysis are inclusion in databases of various types and input to various models, as well as response to regulatory agencies. The Empirical Kinetic Modeling Approach (EKMA) requires the type of non-speciated data produced by Method TO-12, i.e., non-methane organic compound (NMOC) concentration data. Use of total organic compound concentration data in this model substantially reduces the cost and complexity of the analysis system by not requiring qualitative and quantitative species identification. However, other uses of data such as urban airshed modeling or risk assessment require accurate concentrations of specific compounds. The user must select appropriate methodology to generate the type of data required to meet program needs.

Method TO-14 is designed to produce accurate qualitative and quantitative data for specific volatile and semivolatile organic compounds. Method TO-14 itself covers only a small list of compounds which were being analyzed by the laboratories which contributed to the formulation of the method. The term "TO-14 analysis" has been applied to analyte lists which range from two compounds to dozens of compounds, and in some cases which are totally inappropriate for the methodology. Both gas chromatography/mass spectrometry and gas chromatography with a variety of detectors are acceptable analytical methodologies. Method detection limits for any of the possible modes of analysis are not given in the method. Various method detection limits have been established by the laboratories which perform the analysis and have validated the methodology, but no criteria for analytical detection limits are included within the method. This lack of definition within the methodology provides flexibility for laboratories which have developed or wish to develop their own methodologies and standard operating procedures, but a laboratory with no prior experience in the area of air toxics analysis which is looking for more definitive guidance in selecting and establishing methodology will not find the specific guidance in Method TO-14. The laboratory performing the analysis must therefore be able to establish that the analytical technique is appropriate for their own list of compounds of interest.

Successful use of canisters in a sampling and analytical methodology requires that: 1) the canister sampler correctly integrate acquired sample over the collection period; 2) compounds of interest can be accurately recovered, concentrated and analyzed; 3) the analyte is stable in SUMMA® canisters; 4) the canister can be adequately cleaned and protected from contamination. Factor 1 is often referred to as sampler certification and is the subject of another recent paper.[3] Other factors that influence the decision to use canisters are the cost of the initial equipment and the cost of shipping canisters to and from the field.

To perform an analysis of a compound in a canister, the compound must have a reasonable degree of stability in the canister and the compound must be volatile enough to have a sufficient vapor pressure in the canister. Analyses for compounds which lack sufficient volatility (such as polynuclear aromatic hydrocarbons and most pesticides) and polar water-soluble compounds (such as ethylene oxide) are frequently requested, even by regulatory agencies. Individual laboratories have information about the stability of compounds in SUMMA®-passivated canisters accumulated over a period of time, but these individual laboratory databases are usually not published and are very seldom generally accessible. Radian, for instance has detection limit and stability data for a wide range of compounds including nonpolar chlorinated compounds and polar alcohols and ketones.

There are further areas to consider in dealing with canister sampling and analysis. To send canisters to the field for sampling, the canisters must be cleaned and be demonstrated to be clean. There is no single universally recognized acceptable procedure for cleaning canisters, just as there is no single accepted criterion for canister cleanliness. Every laboratory has its own procedure for cleaning canisters. Various procedures in different laboratories use vacuum, pressurization, dry gas, humidified gas, heat or avoidance of heat in the cleaning process. Some laboratories apply a criterion in terms of ppbv total carbon to assess cleanliness (eg. 20 ppbv measured using method TO-12), some laboratories use the criterion of $\leq$ 0.2 ppbv per component of interest. The 0.2 ppbv/component criterion is more stringent and requires blanking of a representative

number of canisters used in a sampling program. If possible, it is desirable to avoid performing two analyses per canister: one for a complete analysis for blanking before the canister is sent to the field and another for the analytical determination. However, there is widespread disagreement over which criterion and what frequency of blanking ought to be applied to determine that a canister has been cleaned adequately.

The search for ever-lower detection limits, driven by the use of ambient air measurement data in risk assessment, poses further problems in cleaning canisters and in evaluating the data. In Radian's laboratory, a canister can be cleaned and a blanking analysis can be performed which meets the criterion of ≤ 0.2 ppbv of each of the components of interest. Radian has the capability to clean canisters using hard vacuum and pressure cycles at ambient air and elevated temperature and flow through purge with humidified air. If clean humidified air is put into this canister and the canister is stored for a period of time prior to analysis, we occasionally observe low ppbv levels of some of the compounds which are most commonly observed in the analysis of field samples. The physical chemical processes that occur in canisters containing low concentration volatile organic compounds are not well understood. Radian is currently exploring this phenomenon through a series of studies to evaluate alternative cleaning procedures.

The question of what is "real" data will continue to involve background levels and cleanliness of canisters. If the next step in analytical techniques drives sensitivity to low ppt levels, a corresponding advance in technology and procedures for cleaning canisters must be made.

The apparatus used for canister cleaning is another area of controversy. The type of equipment and the approach used for cleaning can have a dramatic effect on the cleanliness of canisters. Most cleaning equipment currently in use is custom-designed and built by the laboratory which performs the cleaning procedures. Cleaning systems include options for flow through purge, evacuation, pressurization and humidification. There is no canister cleaning system which is presently commercially available. Radian's experience with the ambient, humidified, pressure-vacuum cycle cleaning approach leads to the conclusion that if one canister cleaned in a group is clean using this approach then generally all the canisters will be clean.

The apparatus for cleaning is second only to the sample introduction interface in the variety available and the controversy that has arisen on appropriate use. If the analytical system cannot handle the water, as is the case with certain mass spectrometers, the canister samples must be dried prior to analysis. Samples are usually dried using a Nafion membrane drier. Drying samples prior to analysis is presently an area of technical controversy. One view is that samples should be analyzed exactly as they are returned from the field in order to avoid any potential compromise of sample integrity, while others maintain that drying canister samples has no effect upon the nonpolar hydrocarbons and halogenated hydrocarbons which are usually the compounds of interest. Drying canister samples prior to analysis may not compromise the sample for these analytes and it simplifies the analysis. Various studies support the successful analysis of dried samples for hydrocarbons and halogenated hydrocarbons; however, the effect of the drying techniques on polar oxygenated compounds has not been thoroughly explored. Current experience at Radian suggests that whole samples (not dried) can be successfully concentrated using a silanized glass bead cryotrap and injected into either a GC/MD or GC/MS system resulting in the successful analysis of nonpolar compounds plus many polar compounds including ethanol, isopropanol, acetone, and 1,4-dioxane.

An additional area of controversy is the question of pressurized canisters versus canisters sampled and analyzed at subambient pressures. Water condensation may occur in 6L canisters if samples are collected and pressurized to positive gauge pressures. The presence of water in the condensed phase may affect the compounds present in the canister: the effect on nonpolar compounds may be slight but, polar compounds will dissolve in the water. If samples are collected in evacuated canisters which are never pressurized with humid air prior to analysis, there is no problem with water in the condensed phase.

Use of GC Multidetector versus GC Mass Spectrometer Analysis

Accurate quantitation of compounds in samples taken either with sorbents or in canisters is an important facet of the quality of these measurements. The decision between selecting gas chromatography/multiple detector (GC/MD) and gas chromatography/mass spectrometry (GC/MS) affects the accuracy of measurements and presents the classic conflict between sensitivity and specificity, with economics frequently the deciding factor. The gas chromatography/mass spectrometry technique offers the generation of the characteristic mass spectra of the analytes for unambiguous identification. GC/MS identification can even provide isomer-specific characterization when a capillary retention time is coupled with mass spectrometric data. The gas chromatographic analysis, on the other hand, offers generally higher sensitivity than the mass spectrometer.

When a laboratory first begins to perform air toxics analysis, deciding between GC/MD and GC/MS is difficult if only one can be chosen. The optimal situation is to have both techniques available, if both can be purchased. In general, a GC/MS system costs significantly less than a GC/MS. A choice among mass spectrometric systems is also not straightforward. The systems which offer the lowest cost are the Mass Selective Detector and the Ion Trap Detector. These systems may have difficulty accommodating the amount of water present in a canister sample of ambient air and therefore the range of analytes that can be determined by this technique is restricted.

Economic considerations very frequently drive a choice of methods when commercial analysis is being performed. A need to characterize components of the sample other than the calibration compounds will determine that mass spectrometry must be used. A requirement for very low detection limits will frequently determine that GC/MD must be used. It occasionally happens that GC/MD is selected as the analytical method because of cost, but when sampling and analysis are performed, the question of coelution arises. To aid in the resolution of problems with coelution, a system of multiple detectors is frequently used for gas chromatographic analysis of volatile organic compounds from SUMMA® polished canisters. At present, most of the multiple detector gas chromatographs which are used in the analysis of ambient air are custom-designed and assembled in the laboratories which use them. Common combinations of detectors include FID, PID, and either HECD or ECD.

After a sample has been analyzed and no more sample is available for reanalysis, a question of coelution can be resolved only by resampling and reanalysis, using a different column or a different analytical technique for the repeated effort.

Sensitivity and Detection Limit

Sensitivity or detection limit is often a concern in canister sample analysis. For a standard sample injection size, sensitivity with GC is largely dependent on the type of detector used for the analysis. With standard GC techniques the choice of detectors includes flame ionization (FID), photoionization (PID), electron capture (ECD), or halogen electrolytic conductivity (HECD). In the case of the electron capture detector, the sensitivity can be as much as three orders of magnitude higher than other detectors. However, standard the gas chromatographic detectors cannot identify an unknown compound and, in most cases, cannot distinguish two compounds which coelute.

Mass spectrometry can be used as a specialized detector but usually GC/MS sensitivity is lower than standard GC detectors. Optimum sensitivity in the mass spectrometric technique requires the use of Selected Ion Monitoring (SIM), which increases sensitivity for the technique at the cost of limiting the information which can be obtained. When SIM is used in mass spectrometry, the instrument does not scan the full mass range. Instead, the instrument focuses only on the masses of interest, and no other information is acquired. The mass spectrometer increases its sensitivity at the cost of being able to identify unknown compounds.

Calibration

Calibration of analytical systems for canister samples further raises questions. Calibration standards should be contained in the same matrix as the samples, so gaseous canister calibration standards should be used to calibrate instruments used for gaseous canister sample analysis. To be consistent between calibration and analysis, the analyst needs to have gaseous calibration standards available in a cleaned canister. The preparation of accurate gaseous calibration standards is a non-trivial matter. For typical water analyses commercially-prepared standards in methanol are available and are readily diluted. For gaseous standards, there are very few commercial sources for a limited number of compounds. Dry certified standard mixtures require custom preparation and are expensive and, depending upon the exact mixture of compounds requested. These standards can require 8-16 weeks or more to prepare and certify.

Humidified working standards of mixtures of gaseous compounds are not commercially available. Individual laboratories usually prepare these standards from neat solutions or from certified standards in dry nitrogen. The typical calibration curve is five points (zero plus four other points) over the concentration range of interest. The cylinder of gaseous standards which has been purchased must be diluted. It is not always possible to incorporate all of the compounds of interest in a single cylinder, so two or more cylinders may be necessary. The contents of the cylinders must be blended and diluted appropriately. Here is another major challenge: there are few commercially available pieces of equipment designed to accept certified cylinders of gaseous standards which generate combined, diluted, humidified, standards in the correct concentrations. Laboratories which use cylinder standards to prepare calibration standards have designed and constructed equipment to perform this function.

Other modes of calibration besides dynamic dilution are certainly possible. Permeation tubes with an appropriate vacuum system for transfer of gas can be used. A permeation system is expensive to construct, and permeation tubes must be prepared, calibrated, and maintained. Preparing canister standards from liquid standards can be done, but the reproducibility and accuracy of the standards prepared by this method is generally lower than the reproducibility and accuracy of gaseous standards prepared by flow dilution. This process can also be quite tedious when more than a few target analytes are needed in the mix. It is possible to be accurate and reproducible with liquid standards, but considerable effort must be expended to acquire the skill and proficiency needed. In Radian laboratories, our proficiency in the analysis of external audit samples tracks directly against our proficiency in preparation of standards. Dynamically diluted standards have always produced better results for Radian than standards prepared from liquid.

The exact method of calibration and addition of internal quantitation standards is another area which raises extensive questions in the analysis of canister samples. Adding a standard to the canister is undesirable because the canister must be handled and some standard compound must be added to the atmosphere inside the canister. A possibility for contamination exists every time a sample must be handled. A way of adding internal standards to the canister sample without risking compromising the integrity of the canister air sample is an area of method development. Presently, many laboratories use an external standard calibration, or internal standards are added at the time that cryogenic trapping of the sample occurs.

With all of the technological challenges that canisters offer to a sampling and analytical laboratory, they offer the advantage of a potentially unchanged field atmosphere for analysis. All sorbent media concentrate organic compounds and therefore change the original atmosphere. Canisters also offer the advantage of replicate sample analysis. Unsuccessful attempts to apply sampling and analysis techniques are not reported in the literature; the standard procedure is to find or develop a methodology which does work. The result of this approach is that new environmental analytical laboratories are frequently in the position of demonstrating repeatedly that something will not work, either because the method is not under control or because compounds which are inappropriate for the canister methodology have been unknowingly requested. Negative results are frequently as important as positive results in this context, and experience unfortunately often comes from repeating the mistakes of others.

SUMMARY

A variety of the canister and sorbent methods for sampling and analysis of ambient air have been discussed. The sampling and analysis of ambient air for volatile organic compounds is an area which is still relatively immature, in spite of the fact that there are laboratories which have been working in this area for twenty years or more. Neither the equipment which is commercially available nor the methodology is yet at the level of completion and availability of methods for sampling and analysis of water. Methods for sampling and analysis of air are, at present, general guidance methods rather than explicit methods which exactly detail procedures, requirements, and compounds to which the methodology is applicable.

Ambient air sampling and analysis requires great care with materials and equipment. Sampling media such as sorbents and canisters can be very costly and, if materials are not handled correctly, very costly sampling trips and series of analyses can be completely invalidated because of contamination, presence of artifacts, or other problems. Necessary field and laboratory equipment is sometimes not commercially available: laboratories wishing to perform the work must design and construct their own equipment or purchase equipment from another group which has designed and built equipment. However, the technology is advancing, equipment will become available in the future, handling and packaging of materials will improve, and procedures will become better-defined. The progress in these areas will require extensive commitment to resource and method development and validation. No matter what the technical and technological progress, there will still be an abundance of problems and traps for the unwary and those who are not sufficiently experienced.

DISCLAIMER

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TABLE 1. TENAX® SAMPLING MEDIUM

Methods	Application	Advantages	Disadvantages
TO-1 Ambient VOST	Volatile, nonpolar organics B.P. 80° - 200° C	1) Compact sampling tubes, especially stainless steel. 2) Easy to handle and ship. 3) Analytical equipment commercially available. 4) May use standards in methanol solution or dilution bulb. 5) Field-ready tubes can be purchased 6) Low Detection Limits by concentrating large sample volumes.	1) Polymer contaminates easily. 2) Breakthrough volumes largely unknown. 3) "One-Shot" analysis. 4) Analysis produces artifacts. 5) Distributed volumes backup tube(s) required. 6) Low breakthrough for very volatile compounds. 7) Samples contain water. 8) Cost due to the need for distributed volume sampling and analysis.

TABLE 2. SUMMA® POLISHED CANISTER SAMPLING MEDIUM

Methods	Application	Advantages	Disadvantages
TO-12, TO-14	Volatile and Semi-Volatile Organic Compounds	1) Canister allows multiple analyses. 2) Can be screened, diluted. 3) Rugged for field handling, shipping. 4) Field-ready canisters, sampling equipment can be rented. 5) Sampling can be done without power. 6) Samples as taken accurately represent field atmosphere. 7) No need to collect distributed volume samples (no breakthrough).	1) High initial cost to purchase. 2) Much of the equipment required to support canister use is not commercially available. 3) Canisters are bulky to ship. 4) Canisters may produce analytical artifacts. 5) Samples contain a large amount of water. 6) Higher detection limits than most sorbent methods.

TABLE 3. CARBON MOLECULAR SIEVE (CMS) SAMPLING MEDIUM

Methods	Application	Advantages	Disadvantages
TO-2	Highly volatile, nonpolar organics; B.P. -15° -120° C	1) Captures gases, very highly volatile compounds. 2) Compact stainless steel sampling tubes; easy to ship and handle. 3) May use standards in methanol solution (commercially available) or static dilution bulb. 4) Field-ready tubes can be purchased. 5) Low detection limits.	1) Requires separate sampling and analysis to cover the range of organic compounds from B.P. -15° C to 200° C. 2) Must be desorbed at 350° - 400° C. 3) Analytical reproducibility varies. 4) Easily contaminated. 5) "One-Shot" analysis.

TABLE 4. POLYURETHANE FOAM (PUF) SAMPLING MEDIUM

Methods	Application	Advantages	Disadvantages
TO-4, TO-9, TO-10, TO-13	Organochlorine pesticides, PCBs, dioxins, furans, polynuclear aromatic hydrocarbons	1) Extract allows dilution, concentration, repeated analysis. 2) High volume sampling (~200-280 L/min).	1) Field preparation is a complicated process. 2) Easily contaminated. 3) Collection efficiency must be determined by user. 4) PUF/XAD-2® not commercially available as a "sampling cartridge". 5) Sampling equipment expensive. 6) Breakthrough for more volatile compounds.

TABLE 5. XAD-2® SAMPLING MEDIUM

Methods	Application	Advantages	Disadvantages
Semi-VOST TO-13 No ambient	Semi-volatile organic compounds (polar and nonpolar)	1) Extract allows dilution, concentration,repeat analyses. 2) Applicable to a very wide range of compounds.	1) Produces 'analytical artifacts. 2) Easily contaminated. 3) Requires careful cleaning. 4) Not commercially available "sampling cartridge". 5) Extensive recovery, detection limit data not available. 6) No official status as a "method"; data not universally accepted.